SHORT PAPER

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Efficient and selective epoxidation of alkenes by supported manganese porphyrin under ultrasonic irradiation[†]

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Alkens are transformed to their corresponding epoxides in high yields and with high selectivity by ultrasonic irradiation and sodium periodate in the presence of catalytic amounts of manganese porphyrin supported on Amberlite IRA-400 ion-exchange resin (MnTPPS-Ad).

Many efficient biomimetic systems for alkene epoxidation using iron and manganese porphyrins as catalysts, and various oxygen atom donors such as PhIO,[1] ClO^-,[2] H_2O_2,[3] ROOH[4] or IO_4^-[5] have been reported previously. The high efficiency of some of these catalytic systems makes them potentially useful for large-scale oxidations. Immobilization of expensive metalloporphyrin catalysts on insoluble organic and inorganic supports appears to be a good way to render them practicable and improve their stability, selectivity and show other advantages with respect to recovery and reuse.[6–12] However, the activity of such heterogeneous catalysts is often less than that of soluble ones, due to either chemical or diffusional restrictions. The successful applications of ultrasonic irradiation in a number of heterogeneous reactions,[13–15] prompted us to study the effect of ultrasonic irradiation on oxygenation reactions catalysed by supported metalloporphyrin catalysts which are usually easy to handle but less reactive.

This communication describes a new periodate-heterogenized metalloporphyrin system for alkene epoxidation in CH_3CN/H_2O mixture under air and ultrasonic irradiation at room temperature. The catalytic activity of the MnTPPS-Ad under ultrasonic irradiation is comparable to the previously described homogeneous manganese porphyrin-periodate catalytic systems.[5]

The epoxidation of styrene as a typical substrate was investigated in the presence of different oxygen donors and sulfonated manganese (III) tetraphenylporphyrin supported on Amberlite IRA-400 ion exchange resin (MnTPPS-Ad)[16] catalyst. As shown in Table 1, higher activity and stability of the supported catalyst was observed with sodium periodate compared to other oxygen donors under ultrasonic irradiation.

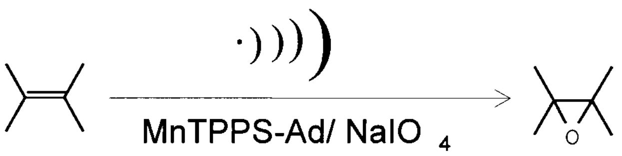
Table 1 Catalytic epoxidation of styrene by MnTPPS-Ad with different oxygen donors[a]

Entry	Oxygen donor	Time/min	Epoxide/%[b]	
			U[c]	S[c]
1	$KHSO_5$[d]	30	90	30
2	NaOCl	60	80	28
3	$NaIO_4$	60	92	31

[a]Reaction conditions: styrene (1 mmol), oxygen donor (2 mmol), imidazole (0.2 mmol), catalyst (mass equiv. to 0.0147 mmole Mn), CH_3CN/H_2O (10 ml/5 ml). [b]GLC yield based on starting styrene. [c]U: ultrasonic irradiation (40 kHz), S: stirred magnetically (1200 rpm). [d]Instead of 10 ml H_2O, 10 ml of phosphate buffer at pH=7 was added.

The effect of different common organic solvents such as CH_3CN, $(CH_3)_2CO$, CH_3OH, CH_3CN/H_2O and $(CH_3)_2CO/H_2O$ on epoxidation of styrene with sodium periodate in the presence of supported manganese porphyrin was also studied. The same rate enhancement was obtained in all of these solvents under ultrasound irradiation. Among these solvents, CH_3CN/H_2O (2/1) mixture, which showed higher epoxide yield, was chosen as the reaction medium.

The effect of different axial ligands upon the epoxidation rate of styrene was also investigated. The epoxidation rates decrease in the order: imidazole = 1-methylimidazole > *t*-butylpyridine > 4-methylpyridine > pyridine. Reactions were performed at room temperature under ultrasonic irradiation in a CH_3CN/H_2O medium containing the alkene, oxidant, imidazole and MnTPPS-Ad in 1: 2: 0.2: 0.0145 ratio, respectively. Under these conditions, various alkenes are converted to their corresponding epoxides in good yields (Table 2, Scheme 1). Reactions were monitored by GLC and the identity of pure epoxides was confirmed by ^1H NMR and MS spectral data. Epoxidation of cyclohexene in the presence of ultrasound led to the formation of cyclohexeneoxide with relatively good selectivity (91%), whereas lower yield and selectivity were observed for the same reaction under agitation using magnetic stirrer. In the case of stilbenes, *trans*-stilbene is converted only to the *trans*-epoxide but *cis*-stilbene to a mixture of *cis*- and *trans*-epoxides. The observed regioselectivity for epoxidation of R-(+)-limonene is higher than that observed for manganese(III) tetraphenylporphyrin with PhIO.[17] The ratio of 1,2-epoxide / 8,9-epoxide was 2. In the absence of the supported metalloporphyrin catalyst, cyclohexene remained almost unchanged by $NaIO_4$ in CH_3CN/H_2O after 24 h.



Scheme 1

The solutions remained colorless during the course of epoxidations and there was no evidence for leaching of the catalyst from support into solution. The attachment of metalloporphyrin to the amberlite made it possible to remove the stable catalyst by simple filtration at the end of the reaction. The stability of the MnTPPS-Ad was also studied in repeated epoxidation reactions of styrene (5 times) with sodium periodate. The catalyst was removed after each reaction by simple filtration and washing with acetonitrile. The reused catalyst dis-

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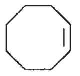
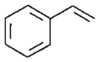
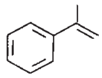
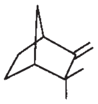
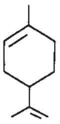
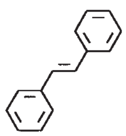
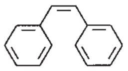
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Epoxidation of alkenes with periodate using MnTPPS-Ad in the presence of imidazole at room temperature[a]

Entry	Alkene	Conversion(%)[b]		Epoxide(%)[d]	
		(U)[c]	(S)[c]	(U)[c]	(S)[c]
1		97	38	97	38
2		96	41	91	31
3		95	37	92	31
4		100	42	93	34
5		80	32	80	32
6		79	27	55(1,2-Epoxide)[d] 24(8,9-Epoxide)[d]	16(1,2-Epoxide)[d] 11(8,9-Epoxide)[d]
7		50	18	50(*trans*-Epoxide)[d]	18(*trans*-Epoxide)[d]
8		79	29	74(*cis*-Epoxide)[d] 5 (*trans*-Epoxide)[d]	26(*cis*-Epoxide)[d] 3(trans-Epoxide)[d]

[a]Reaction conditions : alkene (1 mmol), $NaIO_4$ (2 mmol), Imidazole (0.2 mmol), catalyst (mass equiv. to 0.0145 mmol Mn), CH_3CN/H_2O (10 ml/5 ml), Time (1 h). [b]GLC yield based on starting alkene. [c]U, ultrasonic irradiation(40 kHz). S, stirred magnetically (1200 rpm). [d]Both ^1H NMR and GLC data confirmed the reported yields.

Table 3 Recycling data for supported manganese porphyrin catalysts in the epoxidation of styrene under ultrasonic irradiation[a]

Entry	Conversion / %[b]	Epoxide / %[b]	Mn leached %[c]
1	100	94	2.2
2	95	89	2.1
3	91	86	1.2
4	88	82	1.2
5	86	80	1.1

[a]Reaction conditions: identical with those in Table 2, footnote a. [b]GLC yield based on starting styrene. [c]Reaction solutions assayed for leached Mn using atomic absorption spectroscopy and expressed as percentage of Mn originally present on resin.

played consistent reactivity and selectivity. The yield and leaching data obtained are listed in Table 3.

Our results show that ultrasonic irradiation of the heterogenous Mn-porphyrin / $NaIO_4$ system have two important advantages over those carried out under agitation with a magnetic stirrer. The first is that oxidations are faster, typically complete within 1 h compared to at least 4 h required for agitation. Secondly, generally observed side reactions such as double bond cleavage and allylic oxidation are minimized. Further work concerning the extension of this reaction to various metalloporphyrin catalytic systems is currently under way.

Experimental

All olefins were purified to use by passage through a column of basic alumina and then checked by gas chromatography. The porphyrin ligand, H_2TPP, was prepared and metalated according to the literature procedures.[18,19] MnTPPS immobilized on Amberlite IRA-400 was prepared according to reported procedures[16] (9 μmol of MnTPPS were immobilized on 100 mg of the resin).

General procedure for alkene epoxidation catalyzed by MnTPPS-Ad: All of the reactions were carried out at room temperature under ultrasonic irradiation (Walker Laboratory Cleaner, 200 W, 40 kHz) in a 25 ml flask. A solution of $NaIO_4$ (2 mmol) in H_2O (5 ml) was added to a mixture of alkene (1 mmol), MnTPPS-Ad (14 μmol) and imidazole (0.2 mmol) in CH_3CN (10 ml). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH_2Cl_2 (20 ml) and filtered. The resin was thoroughly washed with CH_2Cl_2 and combined washings and filtrates were purified on silica gel plates or a silica gel column. IR and ^1H NMR spectra data confirmed the identities of the products.

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References

1 J.T. Groves and T.E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 5786.

2 H. Amatsu, T.K. Miyamoto and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3193.

3 T. Hirao, M. Ohno and Y. Ohshiro, *Tetrahedron Lett.*, 1990, **31**, 6039.

4 T.G. Traylor, W.P. Fann and D. Bandyopadhyay, *J. Am. Chem. Soc.*, 1989, **111**, 8009.

5 D. Mohajer and S.Tangestaninejad, *J. Chem. Soc., Chem. Commun.*, 1993, 240.

6 D.R. Leonard and J.R. Lindsay Smith, *J. Chem. Soc., Perkin. Trans. 2***,** 1991, 25.

7 T. Mori, T. Santa and M. Hirobe, *Tetrahedron Lett.*, 1985, **26**, 5555.

8 I. Mochida, K. Tsuji, K. Suetsugu, H. Fujitsu and K. Takeshita, *J. Phys. Chem.*, 1980, **84**, 3159.

9 M. Nakamura, T. Tatsumi and H. Tominage, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3334.

10 S. Tangestaninejad, V. Mirkhani and Majid Moghadam, *J. Chem. Soc. Res. (S),* 1999, 722.

11 H. Turk and W.T. Ford, *J. Org. Chem.*,1991, **56**, 1253.

12 F. Pautet and M. Daudon, *Tetrahedron Lett.*, 1991, **32**, 1457.

13 T. J. Mason, *Advances in Sonochemistry* JAI Press Ltd., London, 1993, Vol. 3.

14 J. Ichihara and T. Hanafusa, *J. Chem. Soc. Chem. Commun.*,1989**,** 1843.

15 S. Tangestaninejad and V. Mirkhani, *Chemi. Lett.*, 1998, 1265

16 Y. Satio, M. Mifume, T. Kawaguchi, J. Odo, Y. Tanaka, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull.,* 1986, **34,** 2885.

17 P. Battoni, J. P. Bartoli, M. Reina-Artile, M. Fort and D. Mansuy, *J. Am. Chem. Soc.*,1988, **110,** 8462.

18 E.B. Fleischer, J.M. Palmer, T.S. Srinivastava and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93,** 3162.

19 A. Harriman and G. Porter, *J. Chem. Soc. Farady II,* 1979, **75,** 1532.